

resonance factors, which are said to cause buildup of charge on the amide oxygen atoms, are obviously smaller for diacetamide than for the sum of these effects for two amide molecules. Further studies on the importance of inductive and resonance effects in these systems are now being made.

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Bidentate Nitrate Amine Metal Complexes

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Two series of amine metal nitrates have been synthesized. These are $A_2M(NO_3)_2$, where A = isoquinoline, quinoline, and 2-picoline and M = Co(II), Ni(II), Cu(II), and Zn(II), and $(\text{isoquinoline})_4M(NO_3)_2$, where M = Co(II) and Ni(II). Electronic spectra, infrared spectra, magnetism, conductivity, and molecular weight studies have been carried out. X-Ray powder photographs indicate that all the quinoline complexes are isomorphous. All the bis-amine complexes are assigned a six-coordinate structure involving bidentate nitrate groups. The tetrakis-isoquinoline derivatives have monodentate nitrate groups. The magnetism and spectra are discussed in terms of the proposed structures.

Introduction

There has been considerable interest during the past few years in the chemistry of the nitrate group because of its versatility as a ligand. It can in principle be ionic, covalent monodentate, covalent bidentate, or act as a bridging ligand in a polymer or in a polynuclear molecule. Examples of all these types of behavior are known to occur in simple nitrates.¹

Complex transition metal nitrates which include some other ligand in addition to a covalent nitrate group have not been so well characterized. Complexes with triphenylphosphine² and its oxide,^{3,4} triphenylarsine oxide,³ hexamethylphosphoramide,⁵ benzimidazole,⁶ thiourea,⁷ trimethylphosphine oxide,^{3,8} pyridine N-oxide,⁹ and some dimethylpyridines^{10,11} have been reported recently, but in few cases are the structures known with certainty. An X-ray structural analysis⁸ of dinitratobis(trimethylphosphine oxide)cobalt(II) shows the presence of two bidentate nitrate groups in a *cis* six-coordinate structure. Bidentate nitrate groups have been suggested to occur for various nickel derivatives,^{2,5,9,10} but this has not been proven. As can be seen there are few data relating to amine metal nitrates. Of the complexes to be described here,

dinitratobis(2-picoline)copper(II)¹² and hydrated dinitratobis(quinoline)copper(II)¹³ have been reported briefly before.

Experimental

Preparation.—The bis-amine complexes were prepared by the interaction of the hydrated metal nitrate (1 equivalent) in 2,2-dimethoxypropane with the appropriate amine (2 equivalents). The nitrates were refluxed in the solvent for 0.5 hr. prior to the addition of the amine to ensure the dehydration of the nitrate. The cobalt, nickel, and zinc complexes were recrystallized from acetone or ethanol-2,2'-dimethoxypropane mixtures containing a small amount of the amine. The copper complexes were purified by Soxhlet extraction with dichloromethane. The tetrakis-isoquinoline derivatives were obtained by recrystallization in the presence of a large excess of isoquinoline.

Analyses.—These are listed in Table I. The carbon, hydrogen, and nitrogen analyses were carried out in the microanalytical laboratory of this college under the direction of Mr. Manohin.

Spectrophotometric Measurements.—Near-infrared and visible spectra were obtained with an Optika CF4 double-beam grating spectrometer. Infrared spectra were recorded with a Perkin-Elmer Model 21 instrument using liquid paraffin and hexachlorobutadiene mulls on sodium chloride plates.

Conductivity Measurements.—A Cambridge conductivity bridge was employed. Solutions, measured at room temperature, were not thermostated.

Molecular Weight Determinations.—A Gallenkamp Mod 1 7665K semimicro ebulliometer was used. The instrument was calibrated with Analar benzoic acid. A series of five or six measurements was made over a concentration range of 0.025–0.125 M, and the molecular weight was determined from the slope of the graph resistance of the thermocouple, proportional to temperature, *vs.* concentration. A good straight line was generally obtained.

Magnetic Measurements.—A Newport Instruments magnetic (Gouy) balance (1.5-in. pole pieces) was employed. The magnetic tubes were calibrated with mercury tetrathiocyanato-

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TABLE I
ANALYTICAL DATA

Complex	C, %		H, %		N, %		Metal, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(α -picoline) ₂ Co(NO ₃) ₂	39.0	39.1	3.8	3.8	15.2	15.3	15.9	15.8
(quinoline) ₂ Co(NO ₃) ₂	49.0	49.3	3.1	3.3	12.7	12.8	13.3	13.3
(isoquinoline) ₂ Co(NO ₃) ₂	49.0	49.3	3.1	3.4	12.5	12.6	13.3	13.1
(isoquinoline) ₄ Co(NO ₃) ₂	61.8	61.9	4.0	4.2	12.0	12.3	8.4	8.5
(α -picoline) ₂ Ni(NO ₃) ₂	39.05	39.3	3.8	3.9	15.2	15.1	15.9	15.9
(quinoline) ₂ Ni(NO ₃) ₂	49.0	49.0	3.1	3.0	12.7	12.7	13.3	13.3
(isoquinoline) ₂ Ni(NO ₃) ₂	49.0	49.2	3.1	3.4	12.7	12.5	13.3	13.4
(isoquinoline) ₄ Ni(NO ₃) ₂	61.8	61.8	4.0	3.9	12.0	11.9	8.4	8.35
(α -picoline) ₂ Cu(NO ₃) ₂	38.6	38.8	3.75	3.7	15.0	14.8	17.0	17.3
(quinoline) ₂ Cu(NO ₃) ₂	48.5	48.3	3.1	3.3	12.5	12.3	14.2	14.45
(isoquinoline) ₂ Cu(NO ₃) ₂	48.5	48.6	3.1	3.4	12.5	12.5	14.2	14.5
(α -picoline) ₂ Zn(NO ₃) ₂	38.4	38.3	3.7	3.6	14.9	14.8	17.4	17.1
(quinoline) ₂ Zn(NO ₃) ₂	48.3	48.6	3.1	3.5	12.5	12.4	14.6	14.6
(isoquinoline) ₂ Zn(NO ₃) ₂	48.3	48.1	3.1	3.2	12.5	12.5	14.6	14.9

cobaltate.¹⁴ The measurements were made at various field strengths to exclude ferromagnetism.

X-Ray Powder Photographs.—These were recorded with a 9-cm. diameter photographic camera using Cu K α radiation (Ni filter). The intensities were estimated visually. The quinoline derivatives are isomorphous. The 2-picoline and isoquinoline derivatives all gave different powder patterns. The bisisoquinoline cobalt and nickel derivatives were amorphous as obtained. The d_{hkl}/n values of the quinoline complexes are listed in Table II.

TABLE II
X-RAY POWDER PHOTOGRAPH DATA (d_{hkl}/n)

Q ₂ Ni(NO ₃) ₂ ^a	Q ₂ Cu(NO ₃) ₂ ^a	Q ₂ Co(NO ₃) ₂ ^a	Q ₂ Zn(NO ₃) ₂ ^a
8.91 vs	9.12 vs	8.86 vs	8.96 vs
7.07 vs	7.14 vs	7.04 vs	7.07 vs
5.43 s	5.26 s	5.37 s	5.37 s
4.63 s	4.43 s	4.52 s	4.46 s
4.00 s	3.98 s	4.13 s	4.11 s
3.66 s	3.65 s	3.64 s	3.60 s
3.27 s	3.23 s	3.25 s	3.21 s
2.74 w	2.70 w		2.75 w
2.54 w	2.55 w		2.50 w
2.42 w	2.44 w		2.41 w
2.11 m	2.11 m	2.11 m	2.11 m
2.03 m	2.00 m	2.03 m	2.03 m
1.94 m	1.92 m	1.92 m	1.94 m

^a Q = quinoline; vs, very strong; s, strong; m, medium; w, weak.

Results

Fourteen amine metal nitrates have been studied; these are A₂M(NO₃)₂, where A = 2-picoline, quinoline, and isoquinoline and M = Co(II), Ni(II), Cu(II), and Zn(II), and (isoquinoline)₄M(NO₃)₂, where M = Co(II) and Ni(II). Complexes containing four 2-picoline or quinoline groups could not be obtained; this is in accord with earlier studies.^{15,16}

Tetrakis-isoquinoline derivatives of zinc and copper were also unobtainable. The complexes are soluble in organic solvents such as the alcohols, chloroform, benzene, acetone, and dichloromethane, but to varying extents, the copper complexes being least soluble. The 2-picoline derivatives are the most sensitive to

traces of water in the solvents or in the atmosphere, hydrolysis being facile. Complexes with the other amines are more stable in this respect. Molecular weight, conductivity, and magnetic measurements are listed in Table III, electronic diffuse reflectance spectra and absorption spectra in Table IV. Some X-ray powder photograph data are listed in Table II.

Bis-Amine Complexes.—Molecular weight measurements in acetone indicate that the complexes are monomeric in solution. They are nonconductors in this solvent. The electronic absorption spectrum is virtually independent of the solvent in which it is measured, implying that the species in solution is unsolvated. Dinitratobis(isoquinoline)cobalt(II) is also shown to be monomeric in benzene. The other complexes are insufficiently soluble in benzene for an accurate molecular weight determination. We conclude that the species, both in the solid state and in solution, is the monomeric unit A₂M(NO₃)₂.

Tetrakis-Amine Complexes.—The solution spectra of these complexes indicate that they dissociate reversibly in solution, forming the bis-amine derivatives.

Discussion

Bis-Amine Complexes.—Conductivity studies in solution and the infrared spectra of the solid leave little doubt that the nitrate group in these complexes is covalently bound to the metal. A strong band occurs near 1000 cm.⁻¹ which is absent from ionic nitrate spectra.^{17,18}

Three basic structures are possible for the A₂M(NO₃)₂ molecule: (a) square-planar with monodentate nitrate groups, (b) tetrahedral with monodentate nitrate groups, and (c) six-coordinate with bidentate nitrate groups (*cis* or *trans*). The X-ray powder photographs of the bis-quinoline metal complexes (Table II) are so similar that we must conclude that all four complexes are probably isostructural. Even though the powder photographs in the 2-picoline and isoquinoline series were not so similar, it is probably safe to infer that the structures parallel the quinoline series. The

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TABLE III
 MAGNETIC, CONDUCTIVITY AND MOLECULAR WEIGHT MEASUREMENTS

Complex	Color	μ_e , ^a B.M.	Λ ^b	Mol. wt. ^c	
				Found	Calcd. for monomer
(α -picoline) ₂ Co(NO ₃) ₂	Deep red	4.51	22	357	369
(quinoline) ₂ Co(NO ₃) ₂	Deep red	4.55	19	353 ^d	441
(isoquinoline) ₂ Co(NO ₃) ₂	Deep red	4.47	13	445, 414 ^e	441
(isoquinoline) ₄ Co(NO ₃) ₂	Pink	4.93	16	286	700
(α -picoline) ₂ Ni(NO ₃) ₂	Green	3.19	15	364	369
(quinoline) ₂ Ni(NO ₃) ₂	Green	3.20	7	444	441
(isoquinoline) ₂ Ni(NO ₃) ₂	Green	3.10	5	463	441
(isoquinoline) ₄ Ni(NO ₃) ₂	Pale blue	3.15	9	374	700
(α -picoline) ₂ Cu(NO ₃) ₂	Deep blue	1.89	28	372	374
(quinoline) ₂ Cu(NO ₃) ₂	Deep blue	1.88	33	^f	...
(isoquinoline) ₂ Cu(NO ₃) ₂	Deep blue	1.89	13	^f	...
(α -picoline) ₂ Zn(NO ₃) ₂	White	0	24	362	376
(quinoline) ₂ Zn(NO ₃) ₂	White	0	15	357 ^d	448
(isoquinoline) ₂ Zn(NO ₃) ₂	White	0	11	452	448

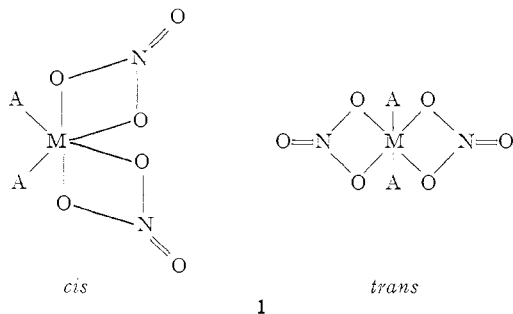
^a Effective moment at 20° calculated from the Curie law; diamagnetic corrections are included. ^b Molecular conductivity (mhos mole⁻¹ cm.⁻²) in acetone (about 10⁻³ M concentration). A 1:1 electrolyte has a molecular conductivity of about 120 mhos mole⁻¹ cm.⁻² in acetone. ^c Ebullioscopically in acetone, see Experimental section. ^d Presumably some amine dissociation occurs in these cases. ^e Molecular weight determined ebullioscopically in benzene. ^f Insufficiently soluble for molecular weight estimation.

 TABLE IV
 THE ELECTRONIC SPECTRA OF (α -picoline)₂M(NO₃)₂ COMPLEXES

Metal	Solvent	Electronic spectrum, cm. ⁻¹ (ϵ)			
Cobalt	D.r.s. ^a			18,250 b	21,020 sh
	Acetone	7425 sh	8850 (16)	18,540 b (154)	
	Dichloromethane	7486 sh	8764 b (15)	18,460 b (125)	
	Benzene		~8800 ^b	18,690 b (146)	20,910 sh
Nickel	D.r.s. ^a			15,710	24,690
	Acetone	8080 sh	8868 (7)	15,530 (20)	24,880 (36)
	Dichloromethane		8812 b (8)	15,680 (26)	24,890 (29)
Copper	D.r.s. ^a			16,140 b	
	Acetone			15,170 b (68)	

^a D.r.s. = diffuse reflectance spectrum. The spectra of the complexes with quinoline and with isoquinoline are not greatly different from those quoted above (see also Figure 1). ^b Solvent absorption in this region.

X-ray data lead us to assume that the stereochemistry is basically the same for all the bis-amine complexes. Making this assumption, the only structure which can be rationalized with all the physical data is (c), six-coordinate with bidentate nitrate groups (1). A square-planar structure is not reconcilable with the



magnetism of the nickel complexes, nor is it a likely stereochemistry for a zinc complex. A tetrahedral stereochemistry is not reconcilable with the spectra of the nickel complexes or of the copper complexes (complexes thought to contain tetrahedral copper do not have absorption near 700 m μ ^{19,20}).

A six-coordinate structure can be rationalized with

all the data. The electronic spectra of the cobalt derivatives are rather intense for a regular octahedral arrangement, but are similar to the spectrum of ((CH₃)₃PO)₂Co(NO₃)₂, known to be six-coordinate.⁸ In the nickel spectra, the intensities are lower and more typical of octahedral complexes. The magnetic moments of the cobalt derivatives lie in the range 4.47–4.55 B.M., similar to a value of 4.65 B.M. found for the trimethylphosphine oxide complex.³ The magnetic moments of the nickel derivatives lie in the range 3.1–3.2 B.M., typical for octahedral nickel. The magnetism and spectra of the copper derivatives are not very characteristic but indicate a planar or six-coordinate environment, rather than a tetrahedral environment.

Tetrakis-Amine Complexes.—These have diffuse reflectance spectra typical of octahedral stereochemistry. The infrared data indicate that the nitrate groups are coordinated to the metal. An octahedral structure is assumed for the solids. Both complexes have magnetic moments typical for octahedral derivatives.

Infrared Spectra.—The nitrate absorption was identified by comparison with the spectra of the corresponding amine cobalt bromides and iodides.^{15,21} The in-

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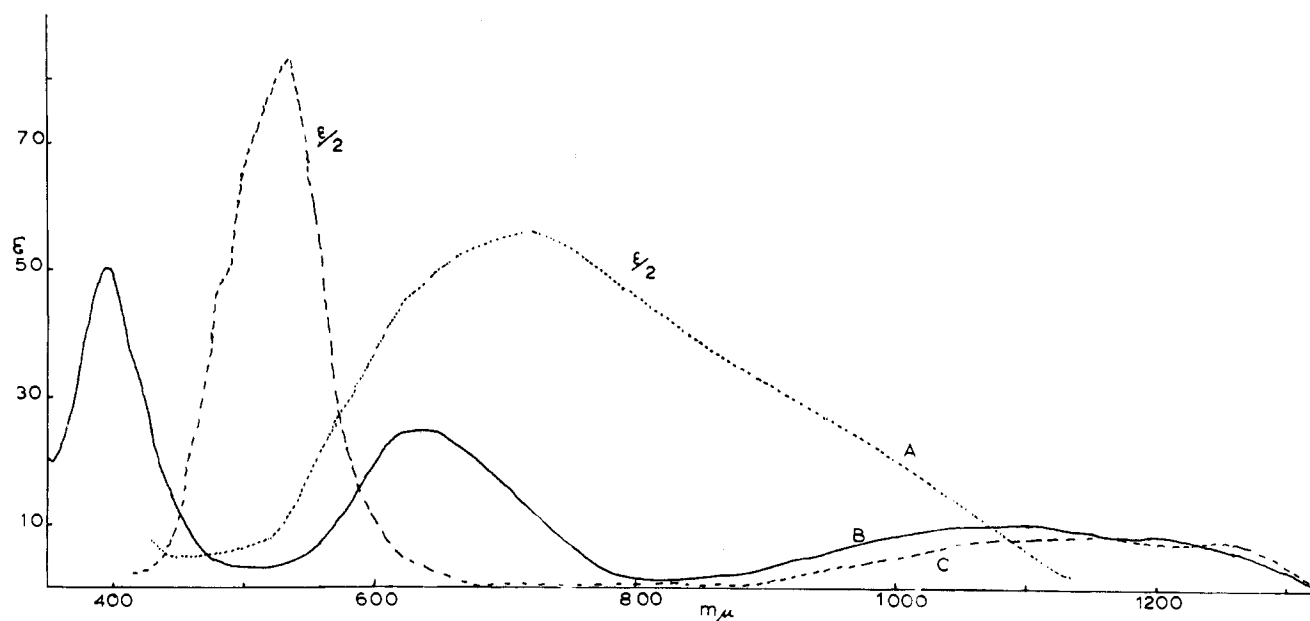


Figure 1.—Absorption spectra in acetone: A, (isoquinoline)₂Cu(NO₃)₂; B, (isoquinoline)₂Ni(NO₃)₂; C, (isoquinoline)₂-Co(NO₃)₂. The cobalt and copper complexes are drawn at half their actual intensity.

frared data may be summarized, using the assignments of Addison and Simpson,²² as follows (cm.⁻¹): ν_1 NO stretch, 1484–1517; ν_2 NO₂ symmetric stretch, 1000–1020; ν_3 NO₂ symmetric bend, 803–824; ν_4 NO₂ asymmetric stretch, 1258–1305; ν_5 NO₂ asymmetric bend, 741–757; and ν_6 out-of-plane rock, 694–720.

Bidentate nitrate groups occur in various unsubstituted metal nitrates including, for example, Ti(NO₃)₄,²³ Cu(NO₃)₂,²⁴ and some uranyl nitrates.^{25,26} It has been suggested that the highest energy absorption of bidentate nitrate groups (ν_1) occurs^{1,27} in the range 1565–1620 cm.⁻¹, and the next absorption (ν_4) in the range 1170–1270 cm.⁻¹. However, there are exceptions to this generalization, since the highest energy nitrate absorption in the trimethylphosphine oxide cobalt complex⁸ occurs at 1517 cm.⁻¹. It is probable that the rule applies only to complexes in which the nitrate group is the only ligand (except perhaps oxygen). The spectra of the complexes described here, which differ little among themselves, are similar to the spectrum of the trimethylphosphine oxide derivative. The tetrakis-amine complexes, having monodentate nitrate groups, are rather different (ν_1 1429 (Co), 1425 (Ni); ν_4 1294 (Co), 1295 (Ni) cm.⁻¹).

The difference between the ν_1 and ν_4 frequencies ($\Delta\nu$) has been used in the past^{1,3} as a guide to the covalent nature of the nitrate group; the greater the difference, the more covalent the bonding. The difference ($\Delta\nu$) is certainly far less in the tetrakis-amine derivatives (130, 135 cm.⁻¹) than in the bis-amine derivatives (187–253 cm.⁻¹). The value of $\Delta\nu$ lies

in the sequence Ni > Co > Cu > Zn for all the bis-amine complexes. The low position of Zn is to be expected, indicating a fairly ionic complex; the relatively low position of Cu may reflect the tendency of that ion to prefer to coordinate to nitrogen rather than to oxygen.

Electronic Spectra.—The visible spectra of the bis-amine nickel complexes appear typical for octahedral compounds involving a fairly high crystal field strength. However, the near-infrared absorption is strongly split (Figure 1) into at least two components derived from the lower symmetry. Dinitratotetrakis(isoquinoline)nickel(II) has a somewhat higher crystal field strength (all the bands have moved to higher energy), as would be expected since an oxygen atom from each nitrate group has been replaced by a nitrogen atom. The near-infrared absorption is not split.

Aside from the intensity, which is rather high, the visible spectra of the bis-amine cobalt complexes are similar to those derived from octahedral complexes. The near-infrared spectra, however, consist of at least two bands. The spectra are also consistent with tetrahedral symmetry if we assume a fairly high value for the Racah parameter (about 850 cm.⁻¹).

Since the spectra and magnetism of ((CH₃)₃PO)₂(NO₃)₂ are consistent with tetrahedral symmetry, Cotton suggests that although the complex is six-coordinate^{3,8} it is possible to visualize the complex as being in a rather distorted quasi-tetrahedral form with bonds directed toward the centers of the nitrate groups instead of toward the oxygen atoms. The assumption of a quasi-tetrahedral structure is perhaps unnecessary. The molecule has a distorted six-coordinate structure and approximate C₂ symmetry. The degeneracy of the ground state of the cobalt ion will be lifted (⁴T_{1g}(O_h) → ⁴A, 2⁴B in C₂). The new ground state being an orbital singlet will give rise to a magnetic

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moment much closer to the spin-only value than that observed in an octahedral complex, and the moment would probably be temperature independent. This is observed.³ The absence of a center of symmetry could produce a fairly high intensity electronic spectrum (since both p and d orbitals span common representations in C_2); this is also observed. The method of distinguishing octahedral from tetrahedral cobalt complexes by magnetic measurements is really only a way of distinguishing an orbital triplet ground state from an orbital singlet ground state. The fact that a cobalt complex has a magnetic moment between 4 and 4.8 B.M. implies that it probably has an orbital singlet ground state, rather than that it is necessarily tetrahedral.

The amine cobalt nitrates have spectra which differ slightly from the trimethylphosphine oxide complex in that there is no weak absorption near 850 $m\mu$. Surprisingly, the spectra are very closely similar, both in wave length and intensity, to the spectrum of the $Co(NO_3)_4^{2-}$ ion,^{28,29} recently shown to be eight-coordinate³⁰ with approximate C_{2v} symmetry. This would also have an orbital singlet ground state, thus explaining its magnetic moment of 4.5 B.M.²⁸ (4.67 B.M.²⁹). Of course there is no obvious way of assigning an eight-coordinate structure to the amine cobalt nitrates, but it does suggest that these complexes could have C_{2v} symmetry. This could be derived from structure **1** (*cis*) by twisting the nitrate groups to generate two new planes of symmetry, or, and this is perhaps more reasonable, from a tetrahedral structure in which two of the positions are occupied by bidentate nitrate groups.^{31,32} Structural models indicate that there is surprisingly little difference in appearance between

the *cis* structure **1** and a C_{2v} molecule derived from a tetrahedron. The distortion in going from one to the other is very small. The nickel complexes also fit into this scheme; the ground state in an octahedral field is an orbital singlet giving rise to moments near the spin-only value. In C_{2v} (or C_2) symmetry, the ground state is still an orbital singlet so that the moment will not be appreciably affected. The splitting of the near-infrared band is indicative of the low symmetry of the molecule. The intensity is, however, rather lower than anticipated. Since it is known^{33,34} that tetrahedral nickel derivatives, for example, do not have such intense spectra as their cobalt counterparts, this may be not too serious a discrepancy. The amine copper nitrates have spectra which are also very closely similar to the spectrum of the $Cu(NO_3)_4^{2-}$ ion. No X-ray data are available for this ion, but it is reasonable to assume that it has a very similar structure to its cobalt analog. The solution spectra of the copper complexes differ from the solid spectra in the position of maximum absorption, but in view of the broadness of the band a relatively small change in structure, such as would be expected to occur in a change of state, could give rise to an appreciable shift in the spectrum.

In summary, it is proposed that all the bis-amine complexes have a six-coordinate structure with bidentate nitrate groups. The structure could well be based on a tetrahedron with two of the positions occupied by bidentate nitrate groups. Such a structure is a moderately distorted form of the approximately C_2 *cis* octahedral dinitratobis(trimethylphosphine oxide)-cobalt(II) molecule.

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(31) It is true that a tetrahedral molecule with monodentate nitrate groups would have C_{2v} symmetry, but such a molecule in common with a large number of L_2CoX_2 (or L_2NiX_2) formerly C_{2v} molecules would give rise to typical tetrahedral behavior.^{5,15,16,20,21} The nickel amine and copper amine nitrates do not appear to be tetrahedral, and so we cannot accept such a structure. In addition the infrared spectrum of such a complex might be expected to have a small $\Delta\nu$ value like the $A_4M(NO_3)_2$ compounds.

(32) Considering only the ligating atoms, the *cis* form of **1** also has C_{2v} symmetry, but complexes such as *cis*- L_4MX_2 compounds have approximately octahedral behavior. Moreover, it seems unlikely that a nitrate group would behave as two independent oxygen atoms.

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